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(54) BORON ION IMPLANTATION USING ALTERNATIVE FLUORINATED BORON PRECURSORS, AND FORMATION OF LARGE BORON HYDRIDES FOR IMPLANTATION

BORIONENIMPLANTATION UNTER VERWENDUNG ALTERNATIVER FLUORIERTER BORVORLÄUFER UND BILDUNG GROSSER BORHYDRIDE FÜR DIE IMPLANTATION

IMPLANTATION D'IONS DE BORE UTILISANT DES PRECURSEURS ALTERNATIFS DE BORE FLUORES, ET FORMATION DE GROS HYDRURES DE BORE A DES FINS D'IMPLANTATION

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to improved methods of implanting boron, particularly to methods of implanting boron-containing ions using boron-containing dopant species that are more readily cleaved than boron trifluoride. There is also described herein a process for supplying a boron hydride precursor, a method of forming a boron hydride precursor and to a source of boron hydride precursor.

DESCRIPTION OF THE RELATED ART

[0002] Ion implantation is used in integrated circuit fabrication to accurately introduce controlled amounts of dopant impurities (e.g., boron) into microelectronic device wafers and is a crucial process in microelectronic/semiconductor manufacturing. In such implantation systems, an ion source ionizes a desired dopant element gas ("the feedstock") and the ions are extracted from the source in the form of an ion beam of desired energy. Extraction is achieved by applying a high voltage across suitably shaped extraction electrodes, which incorporate apertures for passage of the extracted beam. The ion beam is then directed at the surface of the workpiece, such as a microelectronic device wafer, in order to implant the workpiece with the dopant impurity and form a region of desired conductivity. Then, the implanted dopant atoms are activated by annealing to form an electrically active doped region.

[0003] Presently, there are upwards of 10-15 implantation steps in the fabrication of state of the art devices. Increasing wafer sizes, decreasing critical dimensions, and growing circuit complexity are placing greater demands on ion implant tools, with respect to better process control, the deliverance of high beam currents at low energies, and a decrease in the mean time between failures (MTBF).

[0004] Boron trifluoride (BF_3) has traditionally been the source of boron dopant impurities. However, BF_3 is problematic in that it requires a significant amount of energy to break the B-F bonds (757 kJ $mole^{-1}$) compared to other dopant species commonly used in ion implantation (e.g., As-H = 274 kJ $mole^{-1}$ and P-H = 297 kJ $mole^{-1}$). As a result, ion sources must run at high arc voltages when implanting boron. High arc voltages create high energy ions that bombard the hot filament or cathode in the ion source region, contributing to sputter erosion and failure of the cathode.

[0005] It was previously reported that nominally 80% of the BF_3 dopant supplied to an ion implanter was vented intact, suggesting that either the BF_3 was not ionized or, if so, the fragments recombined. Clearly, the low ionization of BF_3 at high arc voltages exacerbates an already highly inefficient process.

[0006] Thus, there is a continuing need for providing alternative boron-containing dopant precursors for use as the boron element gas so as to increase the MTBF, the process efficiency and the life of the tool and to decrease the buildup of nonvolatile species at the ion source region.

[0007] Boron cluster implantation is a method for increasing ion implant efficiency at an energy level lower than that required for implant utilizing boron trifluoride. Typical methods of boron cluster implantation use decaborane (B10) and octadecaborane (B18) boron hydride precursors. These precursors are solid at room temperature and have relatively low vapor pressures. Use of these precursors involves sublimation of the precursor material from a remote container and transfer of the resulting vapor along fluid flow lines to a semiconductor tool for cluster implantation. These processes involve the potential adverse side effects of insufficient material flow and condensation. In order to combat the former, the vessels containing the solid sources must be heated to constant and precise temperatures. In order to prevent unwanted condensation, the lines leading to the tool need to be heat traced.

[0008] Boron cluster implantation utilizing decaborane and octadecaborane as precursors presents additional challenges, including those identified below:

- heat tracing the solid container and transfer lines is costly, cumbersome, difficult to implement in an ion implanter, difficult to retrofit and prone to failure;
- unbalanced heat loads can lead to condensation on cold spots that can result in clogging or uneven flow rates;
- excess heat applied to the solid materials can lead to decomposition resulting in impurities and uneven flow rates;
- the flow rate of sublimed materials depends on the available surface area on the vaporizer. Over time, as a solid is depleted and recrystallized, the surface area of the vaporizer decreases, leading to a drop in flow rate over the lifetime of the charged vaporizer;
- metering the amount of material in the tool is very difficult and is based solely on vapor pressure;

- controlling delivery of the material to the tool is difficult and costly;
- the decaborane and octadecaborane materials are expensive; and
- installation of the vaporizer adjacent to the ion source, often done to minimize the issues with installing heat traced transfer lines inside the implanter, is a dangerous practice that can result in safety and code concerns.

[0009] Accordingly, there is a need in the art for new systems, methods and precursors for cluster boron implantation, including a need for improved methods of delivery of precursors for cluster boron implantation to a tool for implantation, which enable easy transport of the precursor to the tool and increased boron ion implantation, as compared to traditional implantation of boron-containing ions.

[0010] US 5,993,766 discloses a system for the storage and delivery of a sorbable fluid. In a preferred aspect, the system is arranged for storage and delivery of B_2H_6. It is disclosed that a boron source in the storage and dispensing vessel may also utilize suitable subfluorides.

SUMMARY OF THE INVENTION

[0011] The present invention relates to a method of implanting boron-containing ions using boron-containing dopant species that are more readily cleaved than boron trifluoride. More specifically, the present invention relates to improving the efficiency, the MTBF and the life of the ion source hardware using boron-containing dopant species that are more readily cleaved than boron trifluoride.

[0012] The present invention relates to a method of implanting boron-containing ions, comprising: vaporizing a liquid boron-containing precursor feedstock to generate vaporized boron-containing dopant species; ionizing said vaporized boron-containing dopant species in a vacuum chamber under ionization conditions to generate boron-containing ions; and accelerating the boron-containing ions by electric field to produce an ion beam to implant boron-containing ions into a substrate, wherein the boron-containing dopant species comprises B_2F_4.

[0013] There are also described herein compositions or reagents comprising a boron-containing dopant species, wherein said compositions or reagents are useful for boron-containing ion implantation. Suitably, the compositions or reagents may consist essentially of species other than BF_3. Alternatively, the compositions or reagents comprise boron-containing dopant species that are readily cleaved at energies less than 700 kJ/mol, preferably less than 650 kJ/mol, even more preferably less than 600 kJ/mol. The fluorinated boron dopant species comprise B_2F_4.

[0014] There are also described storage and delivery vessels suitable for use in delivery of a material to an ion implant source, wherein the vessel comprises boron-containing dopant species as described herein. Suitably, J the vessel is a cylinder. Alternatively, the vessel is a subatmospheric vessel such as those described in U.S. Patent No. 5,518,528; U.S. Patent No. 5,704,965; U.S. Patent No. 5,704,967; U.S. Patent No. 5,935,305; U.S. Patent No. 6,406,519; U.S. Patent No. 6,204,180; U.S. Patent No. 5,837,027; U.S. Patent No. 6,743,278; U.S. Patent No. 6,089,027; U.S. Patent No. 6,101,816; U.S. Patent No. 6,343,476; U.S. Patent No. 6,660,063; U.S. Patent No. 6,592,653; U.S. Patent No. 6,132,492; U.S. Patent No. 5,851,270; U.S. Patent No. 5,916,245; U.S. Patent No. 5,761,910; U.S. Patent No. 6,083,298; U.S. Patent No. 6,592,653; and U.S. Patent No. 5,707,424. Preferred vessels include, but are not limited to, SDS® and VAC® delivery vessels (available from ATMI, Inc., Danbury, CT, USA). Alternatively, the vessel is an ampoule such as those described in U.S. Patent No. 6,868,869; U.S. Patent No. 6,740,586; U.S. Patent Application Serial Number 10/201,518; U.S. Patent Application Serial Number 10/858,509; U.S. Patent Application Serial Number 10/625,179; U.S. Patent Application Serial Number 10/028,743; U.S. Provisional Patent Application Serial Number 60/662,515; and U.S. Provisional Patent Application Serial Number 60/662,396.

[0015] There are also described herein improved microelectronic devices, and products incorporating same, made using the methods and compositions described herein, and optionally, incorporating the microelectronic device into a product.

[0016] Also described herein is a method of forming a boron hydride precursor and a method for supplying a boron hydride precursor. More specifically, there are described boron hydride precursors generated from boron-containing gas for cluster boron implantation. Additionally there is described herein a source of boron hydride precursor.

[0017] There is described herein a method of forming a boron hydride precursor for cluster boron implantation. The method comprises providing a boron-containing gas and inducing conversion of the boron-containing gas to higher order boron-containing clusters.

[0018] There is also described herein a method of supplying a boron hydride precursor for cluster boron implantation. The method comprises providing a boron-containing gas, inducing conversion of the boron-containing gas to higher order boron-containing clusters and supplying the higher order boron-containing clusters to a tool for cluster boron implantation. Suitably, the conversion is carried out in a reactor adjacent to the tool. Alternatively, the reactor is within the tool.

[0019] There is also described herein a boron hydride precursor source, comprising:

a boron-containing gas source;
a reactor adapted for inducing conversion of boron-containing gas from said boron-containing gas source, to higher order boron-containing clusters;
flow circuitry interconnecting the boron-containing gas source and the reactor; and optionally a mass or pressure controller in said flow circuitry.

[0020] There is also described herein a microelectronic device manufacturing facility, comprising a boron hydride precursor source, and a microelectronic device manufacturing tool, coupled in flow communication with the boron hydride precursor source.

[0021] There is also described herein a method of manufacturing a microelectronic device, comprising cluster boron ion implantation with a cluster boron species formed by the method described above.

[0022] There is also described herein a method of cluster boron ion implantation comprising use of a cluster boron species formed by the method described above.

[0023] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and dependent claims.

DESCRIPTION OF THE DRAWINGS

[0024]

Figure 1 is a schematic representation of a boron hydride precursor delivery system.

Figure 2 is a schematic representation of an in-line diborane concentrator.

Figure 3 is a schematic representation of a high pressure reactor, in which the high pressure is created by a constriction in the exit path, such that the boron cluster formation reaction within the reactor occurs at a higher pressure than the pressure within the tool.

Figure 4 is a schematic representation of a heated packed reactor.

Figure 5 is a schematic representation of a reactor with a concentric tube design.

Figure 6 is a schematic representation of a cold/hot reactor.

Figure 7 is a schematic representation of a multiple temperature heated reactor.

Figure 8 is a schematic representation of a reactor that utilizes plasma or electrical discharge and is adapted for use in a system as described herein.

DETAILED DESCRIPTION OF THE INVENTIONAND PREFERRED EMBODIMENTS THEREOF

[0025] The present invention relates to producing ion beams rich in boron-containing ions using alternative boron-containing precursors that are more readily cleaved than boron trifluoride to improve the efficiency, MTBF and the life of the ion implanter.

[0026] Also described herein are methods of forming a boron hydride precursor for cluster ion implantation and a method for supplying such a precursor for use in cluster ion implantation. Additionally, there is described herein a source for boron hydride precursors.

[0027] As used herein, "ion source region" includes the vacuum chamber, the source arc chamber, the source insulators, the extraction electrodes, the suppression electrodes, the high voltage insulators and the source bushing.

[0028] As used herein, "microelectronic device" corresponds to semiconductor substrates, flat panel displays, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications and packaging. It is to be understood that the term "microelectronic device" is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device or microelectronic assembly.

[0029] As used herein, "precursor" includes any molecule or structure that precedes and is the source of another molecule or structure. As such a "boron precursor" is a precursor that contains boron and can be utilized as a source for boron ions in various implantation methods. Similarly, a "boron hydride precursor" is a precursor that contains a boron

hydride and can be a source for boron ions in implantation.

[0030] Boron ions (B^+) are typically implanted to form a p-type region in a silicon substrate however, also contemplated herein is a method of manufacturing a microelectronic device having a shallow p-type doped region, by implanting molecular ions containing boron, as is well known to those skilled in the art. For example, a molecular ion such as BF_2^+ may be implanted in order to attain low effective boron energy at higher extracted energy of the BF_2^+ ion.

[0031] It has been postulated by the present inventors that lowering the bond energy of the boron-containing dopant compound will result in a concomitant lowering of the required arc voltage, thus increasing the life of the ion source.

[0032] Accordingly, one embodiment of the invention comprises ionizing a boron-containing dopant species at a high ionization efficiency of at least 15% using an arc voltage less than 100 volts, preferably less than 90 volts, more preferably less than 80 volts, and most preferably less than 70 volts, using a conventional hot cathode ion source or comparable voltages using another ion source. In one aspect, the boron-containing precursor feedstock is devoid of substantial quantities of boron trifluoride.

[0033] Boron-containing precursors described herein include, but are not limited to, B_2F_4, $B(BF_2)_3CO$, BF_2CH_3, BF_2CF_3, BF_2Cl, $BFCl_2$, $BF(CH_3)_2$, $NOBF_4$, NH_4BF_4, H_2BF_7, $H_2B_2F_6$, $H_4B_4F_{10}$, H_2BFO_2, $H_2B_2F_2O_3$, $H_2B_2F_2O_6$, $H_2B_2F_4O_2$, $H_3BF_2O_2$, $H_4BF_3O_2$, $H_4BF_3O_3$, B_8F_{12}, $B_{10}F_{12}$, $(F_2B)_3BCO$, and combinations thereof. Alternatively, the fluorine atoms of the aforementioned boron-containing precursors may be partially or totally substituted with other halogen atoms (e.g., BCl_3, BBr_3, B_2Cl_4), etc.). Suitably, the boron-containing precursors include B_2F_4, which is expected to undergo homolytic cleavage at the B-B bond at arc voltages that are lower than that needed to cleave the B-F bond in BF_3. Accordingly, another embodiment of the invention comprises cleaving the boron-containing precursor at the B-B bond. The compositions or delivery systems described herein comprise boron-containing precursors having at least one B-B bond.

[0034] Preferably, the boron-containing precursor species require a dissociate energy in a range from about 100 kJ $mole^{-1}$ to about 650 kJ $mole^{-1}$ more preferably 300 kJ $mole^{-1}$ to about 550 kJ $mole^{-1}$.

[0035] In another embodiment, the present invention comprises implanting boron-containing ions into a microelectronic device substrate, wherein the boron-containing precursor feedstock comprises boron trifluoride, B_2F_4 and optionally at least one additional boron-containing precursor selected from the group consisting of $B(BF_2)_3CO$, BF_2CH_3, BF_2CF_3, BF_2Cl, $BFCl_2$, $BF(CH_3)_2$, $NOBF_4$, NH_4BF_4, H_2BF_7, $H_2B_2F_6$, $H_4B_4F_{10}$, H_2BFO_2, $H_2B_2F_2O_3$, $H_2B_2F_2O_6$, $H_2B_2F_4O_2$, $H_3BF_2O_2$, $H_4BF_3O_2$, $H_4BF_3O_3$, B_8F_{12}, $B_{10}F_{12}$, $(F_2B)_3BCO$, and combinations thereof.

[0036] Further boron-containing precursor species include higher order boranes and carboranes, small nido-carboranes such as CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$, and $C_2B_3H_7$; open cage carboranes such as $C_2B_3H_7$, CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$, $C_2B_7H_{13}$; the small closo-carboranes such as $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$, CB_5H_7, $C_2B_6H_8$, $C_2B_7H_9$, $C_2B_8H_{10}$, $C_2B_9H_{11}$, $C_2B_{10}H_{12}$. In addition, derivatives of these carboranes may be used to modify and optimize the chemical properties of the carboranes (i.e vapor pressure, toxicity, reactivity) in combination with a fluorine source. Higher order boranes and carboranes tend to be more stable compounds than the halogenated boron-containing precursors and may provide B_xH_y fragments at lower arc voltages for ion implantation. Optionally and preferably, when the boron-containing precursor species include the higher order boranes and/or carboranes, the boron-containing precursor feedstock includes at least one alternative fluorine source (e.g., F_2).

[0037] In yet another embodiment, the boron-containing precursor may include at least one aforementioned halogenated boron-containing precursor and higher order boranes and/or carboranes, optionally in the presence of a fluorine source.

[0038] In addition to lowering the arc voltage needed to dissociate the boron-containing precursors, the species preferably dissociate into byproducts that are volatile and will not plate the inside of the vacuum chamber and other components of the ion source region. Further, the boron-containing precursors preferably have a low carbon content (i.e., less than 3 carbon atoms per molecule, preferably less than 2, and most preferably less than 1) as carbon deposits tend to shorten the life of the ion source components.

[0039] An advantage of using fluorinated boron-containing precursors includes the generation of fluorine radicals created in the ion source, said radicals reacting with boron deposited on the walls of the ion source region components, thereby keeping said components clean. Towards that end, fluorine-containing species, e.g., F_2, may be introduced to the ion source region during ionization to assist with component and chamber cleaning processes when the fluorinated boron-containing dopant species do not generate enough fluorine radicals during ionization. The amount of fluorine-containing species relative to fluorinated boron-containing dopant species is readily determined by one skilled in the art. Accordingly, one embodiment of the invention relates to a method of implanting boron-containing ions using a boron-containing precursor comprising B_2F_4 optionally in combination with one or more of boron-containing dopant species selected from the group consisting of BF_3, BCl_3, BBr_3 B_2Cl_2, $B(BF_2)_3CO$, BF_2CH_3, BF_2CF_3, BF_2Cl, BFI_2, $BF(CH_3)_2$, $NOBF_4$, NH_4BF_4, H_2BF_7, $H_2B_2F_6$, $H_4B_4F_{10}$, H_2BFO_2, $H_2B_2F_2O_3$, $H_2B_2F_2O_6$, $H_2B_2F_4O_2$, $H_3BF_2O_2$, $H_4BF_3O_2$, $H_4BF_3O_3$, B_8F_{12}, $B_{10}F_{12}$, $(F_2B)_3BCO$, CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$, $C_2B_3H_7$, $C_2B_3H_7$, CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$, $C_2B_7H_{13}$, $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$, CB_5H_7, $C_2B_6H_8$, $C_2B_7H_9$, $C_2B_8H_{10}$, $C_2B_9H_{11}$, $C_2B_{10}H_{12}$, $(Cl_2B)_3BCO$, and combinations thereof, and a fluorine-containing species (e.g., F_2).

[0040] In another embodiment of the invention, noble gases such as neon, argon, krypton or xenon may be co-blended with the boron-containing dopant species, or alternatively separately fed to the vacuum chamber for mixing with the boron-containing dopant species therein, thereby forming a vapor phase reagent composition. Although not wishing to be bound by theory, it is thought that the noble gases will collide with the boron-containing dopant species and assist with the disassociation of the dopant species at lower arc voltages. In addition, the co-blending of the boron-containing precursor with the noble gases makes the operating conditions more benign. Accordingly, in another aspect of the invention, noble gases are added to increase the ionization efficiency.

[0041] It is also contemplated herein that the feedstock includes boron trifluoride, in addition to the boron-containing precursors disclosed herein. For example, the feedstock may include about 0.01 to about 90 percent by weight BF_3, based on the total weight of the feedstock.

[0042] In practice, liquid and optionally solid boron-containing precursor feedstock is vaporized using vaporization methods well known in the art, e.g., reduced pressure, heating, etc., before or at the vacuum chamber, while gaseous precursor feedstock is introduced directly to the vacuum chamber. An ion source generates ions by introducing electrons into the vacuum chamber filled with gaseous dopant species. Several types of ion sources are commonly used in commercial ion implantation systems, including the Freeman and Bernas types using thermoelectrodes and powered by an electric arc, a microwave type using a magnetron, indirectly heated cathode sources, and RF plasma sources, all of which typically operate in a vacuum. Collisions of the electrons with the gaseous dopant species results in the creation of an ionized plasma consisting of positive and negative dopant ions. An extraction electrode with a negative or positive bias will respectively allow the positive or negative ions to pass through the aperture and out of the ion source as a collimated ion beam, which is accelerated towards the microelectronic device workpiece.

[0043] Cluster boron implantation allows an increase in ion implant efficiency, relative to use of traditional boron precursors such as boron trifluoride, boron trifluoride, diborane, and the like. Implanters used in the process can work at lower energies than traditional dopant delivery processes utilizing such boron precursors. Use of cluster technology allows for delivery of multiple borons at one time. There is also described herein a method of forming boron hydride precursors, a source of boron hydride precursors and a method for delivering the boron hydride precursors for boron cluster implantation.

[0044] The boron hydride diborane(6) is a gas that is toxic, flammable, pyrophoric, dangerous and has a repulsive odor. It is known to decompose at room temperature, forming higher order boranes, such as BH_3, B_3H_7, B_4H_8, and the like. Decomposition reactions may include the following:

$$B_2H_6 \rightarrow 2BH_3;$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9;$$

$$B_3H_9 \rightarrow B_3H_7+H_2;$$

$$B_3H_7 + B_2H_6 \rightarrow B_4H_{10} + BH_3;$$

$$B_4H_{10} \leftrightarrow B_4H_8 + H_2; \text{ and}$$

$$B_4H_{10} \leftrightarrow B_3H_7 + BH_3.$$

[0045] Because of its high rate of decomposition, the gas is generally commercially available only at concentrations of 30% or less. This natural decomposition process and the formation of higher order boranes may be utilized to generate boron hydride precursors for use in cluster boron implantation. Preferably the formation of boron hydride precursors is performed in proximity to or at the point of use of the precursors.

[0046] There may be provided a pressure-controlled or flow-controlled borane source, from which the borane source material is introduced as a gas to a reactor for reaction therein to form higher order boron clusters, which then are flowed to a tool for boron cluster implantation, as shown in Figure 1.

[0047] Figure 1 is a schematic representation of a cluster boron delivery process system 10. The boron precursor is contained in a cylindrical vessel 12 having a valve head assembly 14 secured to the upper portion of the vessel. The vessel and head valve assembly are contained in a gas box 16, in which the head valve assembly is coupled with transfer line 18. The transfer line 18 exteriorly of the gas box 16 contains a mass or pressure controller 20 therein to modulate the flow of the boron precursor vapor.

[0048] The cylindrical vessel 12 preferably contains the boron source material in a gaseous state.

[0049] Alternatively, although less preferred, the vessel may contain the boron source material in a solid state, with the vessel being heated in the gas box, to effect volatilization of the solid to form the precursor vapor. The vessel can be heated in any suitable manner (heating components and/or devices not shown in Figure 1), e.g., by use of a heating

jacket, convective heat transfer in the gas box, or in any other manner appropriate to generate the boron precursor vapor in the desired amount.

[0050] The transfer line 18 is coupled at its downstream end to a reactor 22 in which the boron precursor is submitted to process conditions effecting generation of higher order boron species, e.g., higher order boranes, such as BH_3, B_3H_7, B_4H_8, and the like. The reactor 22 as shown is located adjacently to the semiconductor tool 24, with the reactor in fluid supply relationship with the tool, so that the higher order boranes flow directly into the tool from the reactor.

[0051] The reactor may be located separate from, adjacent to or within the tool. The tool can comprise for example an ion implanter unit, or other boron precursor fluid-utilizing tool. Suitably, the tool is a microelectronic device manufacturing tool.

[0052] In preferred practice, the borane source is a gas. Such a boron-containing gas will be easy to transport. The source material, the boron-containing gas, can be stored prior to use in any manner known to those in the art. Such storage methods can include, but are not limited to, neat gas storage, and storage of the gas in a diluted form, in inert gases such as hydrogen, argon, helium or nitrogen. Exemplary borane source gases include, but are not limited to diborane and pentaborane.

[0053] As the borane-containing gas is transferred from the supply vessel to the reactor, it preferably is passed through a controller, such as the mass or pressure controller 20 illustratively shown in Figure 1. Such a controller may regulate mass or pressure, such that the gas remains in its desired state for delivery to the reactor. Such control is an advantage over previous methods which utilized solid material and flow through heat traced lines. Use of a controller is not required, but is highly advantageous in providing a desired flow of precursor gas to the reactor.

[0054] In addition to the borane-containing gas, an additional reactant or reactants may be supplied. Such additional reactants may be added at any point in the transfer from the gas source to the reactor, or may be added to the reactor itself. Such a reactant or reactants can for example be utilized to improve the kinetics or efficiency of the reaction or to form more complex higher order boron species. Use of such reactants can allow optimization of hydrogen to boron ratios to form desired products. For example, formation of non-volatile boron polymers can be inhibited by using a proper H_2 mixture that maximizes the yield of non-clogging materials.

[0055] Where diborane is the gas utilized, the concentration of the diborane gas may range from 1000 ppm to 30% by weight. Original concentrations of a diborane gas greater than 30% are not stable in the storage container and will decompose. When a concentration of grater than 30% is desired to be provided to the reactor, a concentrator may be utilized in the line transferring the gas to the reactor.

[0056] Such a concentrator is schematically illustrated in the precursor delivery system shown in Figure 2, in which a dilute diborane feed stream in feed line 30 is flowed to the H2 Getter/Diborane Concentrator 32, with the resulting concentrated diborane being flowed to the reactor 34 for generation therein of higher order boranes, as discharged from the reactor in discharge line 36.

[0057] In a situation where greater than 30% diborane is desired, the concentrator is utilized to reduce the amount of H_2 in the line. Such reduction of hydrogen can be achieved utilizing H_2 getters or permeation methods, e.g., with a hydrogen permselective membrane being employed for hydrogen removal from the higher order borane species.

[0058] The reactor utilized for generating higher order boranes can be located near the point of use of the resulting clusters. Such a location may be separate from, adjacent to or within the tool for use of the clusters. Within the reactor, a reaction is induced that results in the production of boron molecules with greater than 2 borons present. The temperature of the reaction within the reactor in various embodiments can be within a range of room temperature to 400°C, and pressure within the reactor in various embodiments can be within a range of vacuum to 1000psi.

[0059] For such purpose, various types of reactors can be utilized, within the skill of the art, based on the disclosure herein. Use of any reactor that induces production of boron clusters is possible. Reactors that may usefully be employed include, without limitation, heated reactors, catalytic reactors, heated catalytic reactors, UV lamps, reactors with electric, microwave or radio frequency discharge or plasma, packed reactors, multiple stage heated reactors, hot plates, high pressure reactors and concentric tubular reactors. The types of reactors listed are not mutually exclusive, for example, a heated, packed, catalytic reactor (see Figure 4) or a multiple stage heated, concentric reactor (see Figure 5) can be used.

[0060] A heated reactor usefully employed can include any reactor that is heated. Such reactor can be a heated wall reactor, a heated packed reactor, a cold wall reactor, a reactor with an internally heated section and a reactor containing multiple stage temperature grading throughout the reactor volume. A heated reactor includes any reactor where heat is utilized in induction of the reaction. Heated reactors of various types are illustratively shown in Figures 3-8.

[0061] A catalytic reactor usefully employed can include any reactor that accelerates the reaction within the reactor. Catalysts may be added to the reaction or may be in integrated part of the reactor itself. Catalysts may include, but are not limited to, metals such as iron, aluminum, copper, alumina, platinum, boron, carbon, carbon adsorbent and activated carbon. Where catalysts are a part of the reactor, they may be mounted to structural surfaces of the reactor, packed into the reactor as beads or pellets or the reactor may include a catalyst impregnated media with any known flow design, such as a tube, honeycomb or beading. Catalyst reactors of widely varied types may be employed.

[0062] A high pressure reactor for use in a method or system may include any reactor that allows the reaction to occur

at high pressure. The high pressure may be generated by any method known to those in the art. For example, pressure within the reactor can be generated by the use of an orifice or slit at the exit region of the reactor, such that pressure is built up in the reactor for delivery of the boron-containing clusters to the semiconductor tool. Typically, when the tool is an ion implanter, the pressure within the tool will be a vacuum, e.g., subatmospheric pressure.

[0063] Figure 3 is a schematic representation of a high pressure reactor 40, in which the high pressure is created by a constriction in the exit path 44, such that the boron cluster formation reaction within the reactor occurs at a higher pressure than the pressure within the tool. The reactor has an inlet 42 in which diborane or borane mixtures can be introduced to the reactor interior volume, and reacted therein to form larger boron clusters that are discharged from the reactor outlet. In this reactor scheme, P1 and T1 are greater than P2 and T2.

[0064] A packed reactor for use in a method or system may include any reactor that contains packing material. The packing material can be used simply to increase the surface reaction for the reaction to occur, to improve the heat transfer, or to provide catalytic effect. The packing material may also include a catalyst impregnated media with any known flow design, such as a tube, honeycomb or beading.

[0065] Figure 4 is a schematic representation of a heated packed reactor 50. The reactor has an inlet 60 by which diborane or borane mixtures can be introduced into the reactor interior volume. The interior volume 52 contains a surface area reaction enhancement or is packed with catalyst, and produces larger boron clusters that are discharged from the reactor in discharge line 56.

[0066] A concentric tubular reactor can include any reactor that has multiple tubes. An illustrative example is shown in Figure 5, in which multiple gases are combined for the reaction within the reactor, with the reaction occurring at a critical point in the heated zone.

[0067] The reactor 70 of Figure 5 includes an interior concentric tube 72 that is coaxial with the main casing of the reactor and defines an annular passage therebetween. The annular passage communicates in fluid flow relationship with a reactant(s) feed inlet 74 in which reactant(s) enter in the direction indicated by arrow B. Such introduced reactant(s) at the outlet end of the interior concentric tube 72 mix with the diborane or borane mixtures flowed into the tube 72 in the direction indicated by arrow A. Thermal or plasma energy is introduced to the respective fluid streams that mix in the reaction zone 76 and yield larger boron clusters that are discharged from the reactor 70 at the outlet thereof, being discharged in the direction indicated by arrow C.

[0068] A multiple stage heated reactor can include any reactor that has variation in temperature from one part of the reactor to another. Such reactors may include, but are not limited to, cold/hot reactors, and heated reactors with temperature grading. Such uses of temperature variations may be to maximize the efficiency of cluster conversion rates, or to control the reaction in any desirable manner. For example, the reactor can have a heated zone that is located away from the exit of the reactor, thereby minimizing clogging that might otherwise occur.

[0069] Figure 6 is a schematic representation of a cold/hot reactor 80. The reactor 80 includes an inlet 82 through which the diborane or borane mixtures are introduced to the interior volume 83 of the reactor. The interior volume 83 has a heated zone 84 therein, which may optionally contain a catalyst. The larger boron clusters produced in the reactor 80 are discharged from the reactor at outlet 86.

[0070] Figure 7 is a schematic representation of a multiple stage heated reactor 90. The reactor 90 includes an inlet for introduction of diborane or borane mixtures, schematically represented by arrow A. The reactor features multiple stage temperature grading, to conduct reaction that produces the larger boron clusters that are discharged from the reactor in the outlet schematically indicated by arrow B.

[0071] Figure 8 is a schematic representation of a reactor 94 that utilizes plasma or electrical, microwave or radio frequency discharge and is adapted for use in a system of the invention. The reactor 94 encloses an interior volume 97 into which extends a tubular inlet passage 95 having an electrical or plasma discharge region 96 for inducing reaction producing the larger boron clusters that are discharged from the reactor outlet 98.

[0072] A hot plate may also be used as a reactor in the practice of the invention. On such a reactor, the diborane or other source gas is flash reacted by a surface induced reaction.

[0073] Once formed, the boron clusters can be delivered to a tool for use in cluster boron implantation. Delivery from the reactor to the tool can be effected in any suitable manner. Where the reactor is adjacent to or within the tool, delivery may be effected simply by the cluster boron stream exiting the reactor and passing into the tool.

[0074] There is therefore contemplated a method of forming a boron hydride precursor for cluster boron implantation, comprising providing a boron-containing gas to a reactor and inducing conversion of the boron-containing gas to higher order boron-containing clusters within the reactor.

[0075] The boron-containing gas that is subjected to reaction for formation of higher order boron species can be selected from diborane, pentaborane, and any other suitable boron source reagents, including mixtures of two or more of such source reagent species.

[0076] The reactor may be selected from among heated reactors, catalytic reactors, heated catalytic reactors, UV lamps, reactors containing an electric, microwave or radio frequency discharge or plasma, packed reactors, multiple stage heated reactors, hot plates, high pressure reactors, and concentric tubular reactors. The reactor can further

comprise a catalyst, e.g., iron, aluminum, copper, alumina, platinum, boron, carbon, and activated carbon. The induction of higher order boron-containing clusters can comprise heating the boron-containing gas within the reactor, providing thermal of plasma energy to the boron-containing gas within the reactor, providing multiple stage temperature grading to the boron-containing gas within the reactor, performing the reaction for induction of higher order boron-containing clusters at a temperature in a range of from room temperature to 400°C, and/or pressure in a range of vacuum to 1000 psi. The reaction can be carried out with addition of further reactant(s) to the reactor prior to or concurrent with the formation of higher order boron-containing clusters.

[0077] There is also contemplated a method of supplying a boron hydride precursor for cluster boron implantation, involving providing a boron-containing gas to a reactor, inducing conversion of the boron-containing gas to higher order boron-containing clusters within the reactor and supplying the higher order boron-containing clusters to a tool for cluster boron implantation.

[0078] There is also contemplated a boron hydride precursor source including a boron-containing gas source, a reactor, and a transfer line or other flow circuitry interconnecting the boron-containing gas source and the reactor, optionally containing a mass or pressure controller therein.

[0079] It will be recognized that a wide variety of specific arrangements may be employed for formation of the higher order boron species for delivery to a utilization facility for such species. The utilization facility can be of any suitable type, e.g., including microelectronic device manufacturing tools such as ion implanters, deposition chambers, etc.

[0080] Thus, while the invention has been described herein with reference to various specific embodiments, it will be appreciated that the invention is not thus limited, and extends to and encompasses various other modifications and embodiments, as will be appreciated by those ordinarily skilled in the art.

Claims

1. A method of implanting boron-containing ions, comprising:

vaporizing a liquid boron-containing precursor feedstock to generate vaporized boron-containing dopant species; ionizing said vaporized boron-containing dopant species in a vacuum chamber under ionization conditions to generate boron-containing ions; and accelerating the boron-containing ions by electric field to produce an ion beam to implant boron-containing ions into a substrate, wherein the boron-containing dopant species comprises B_2F_4.

2. The method of claim 1, further comprising annealing the substrate subsequent to implanting the boron-containing-ions into the substrate.

3. The method of claim 1, wherein at least 15% of the boron-containing dopant species is ionized in said ionizing and said ionizing is carried out at arc voltage of less than 100 volts using a hot cathode ion source.

4. The method of claim 3, wherein said ionizing is carried out at arc voltage of less than 90 volts.

5. The method of claim 3, wherein said ionizing is carried out at arc voltage of less than 80 volts.

6. The method of claim 3, wherein said ionizing is carried out at arc voltage of less than 70 volts.

7. The method of claim 1, wherein said boron-containing dopant species is mixed with a noble gas for the ionizing.

8. The method of claim 7, wherein said noble gas is selected from the group consisting of neon and argon.

9. The method of claim 7, wherein said noble gas is selected from the group consisting of krypton and xenon.

10. The method of claim 1, wherein said boron-containing dopant species further comprises BF_3.

11. The method of claim 1, wherein said substrate comprises an article selected from the group consisting of semiconductor substrates, substrates for flat panel displays, and substrates for microelectromechanical systems - MEMS.

12. The method of claim 1, wherein said ionizing is carried out using an ion source.

13. The method of claim 12, wherein said ion source comprises an ion source selected from the group consisting of ion

sources of types using thermoelectrodes and powered by an electric arc, microwave types of ion sources using a magnetron, indirectly heated cathode sources, and RF plasma sources.

14. The method of claim 1, wherein said vacuum chamber includes an extraction electrode and said ionizing is conducted to produce a collimated ion beam of boron-containing ions.

Patentansprüche

1. Verfahren zum Implantieren von borhaltigen Ionen, umfassend:

Verdampfen eines flüssigen borhaltigen Vorläufer-Stoffes, um einen verdampften borhaltigen Dotierstoff zu erhalten;
Ionisieren des verdampften borhaltigen Dotierstoffes in einer Vakuumkammer unter Ionisierungsbedingungen, um borhaltige Ionen zu erzeugen; und Beschleunigen der borhaltigen Ionen mithilfe eines elektrischen Feldes, um einen Ionenstrahl zur Implantation borhaltiger Ionen in ein Substrat zu erzeugen, worin der borhaltige Dotierstoff B_2F_4 umfasst.

2. Verfahren nach Anspruch 1, ferner umfassend eine Wärmebehandlung des Substrats nach Implantation der borhaltigen Ionen in das Substrat.

3. Verfahren nach Anspruch 1, worin mindestens 15% des borhaltigen Dotierstoffes bei der Ionisierung ionisiert werden und die Ionisierung bei einer Lichtbogenspannung von weniger als 100 Volt und unter Verwendung einer eine Glühkathode umfassenden Ionenquelle erfolgt.

4. Verfahren nach Anspruch 3, worin die Ionisierung bei einer Lichtbogenspannung von weniger als 90 Volt erfolgt.

5. Verfahren nach Anspruch 3, worin die Ionisierung bei einer Lichtbogenspannung von weniger als 80 Volt erfolgt.

6. Verfahren nach Anspruch 3, worin die Ionisierung bei einer Lichtbogenspannung von weniger als 70 Volt erfolgt.

7. Verfahren nach Anspruch worin der borhaltige Dotierstoff für die Ionisierung mit einem Edelgas gemischt wird.

8. Verfahren nach Anspruch 7, worin das Edelgas ausgewählt ist aus der Gruppe bestehend aus Neon und Argon.

9. Verfahren nach Anspruch 7 worin das Edelgas ausgewählt ist aus der Gruppe bestehend aus Krypton und Xenon.

10. Verfahren nach Anspruch 1 worin der borhaltige Dotierstoff ferner BF_3 umfasst.

11. Verfahren nach Anspruch 1 worin das Substrat einen aus der Gruppe bestehend aus Halbleitersubstraten, Substraten für Flachbildschirme und Substraten für mikroelektromechanische Systeme (MEMS) ausgewählten Artikel umfasst.

12. Verfahren nach Anspruch 1, worin die Ionisierung unter Verwendung einer Ionenquelle erfolgt.

13. Verfahren nach Anspruch 12, worin die Ionenquelle eine aus der Gruppe bestehend aus Thermoelektroden verwendenden und mit Bogenentladung betriebenen Typen von Ionenquellen, Mikrowellen-Typen von Ionenquellen unter Verwendung eines Magnetrons, Ionenquellen mit indirekt geheizten Kathoden und RF-Plasma-Quellen ausgewählte Ionenquelle umfasst.

14. Verfahren nach Anspruch 1, worin die Vakuumkammer eine Extraktionselektrode umfasst und die Ionisierung durchgeführt wird, um einen kollimierten Ionenstrahl aus borhaltigen Ionen zu erzeugen.

Revendications

1. Procédé d'implantation d'ions contenant du bore, comprenant :

la vaporisation d'une charge de précurseur contenant du bore liquide pour générer des espèces de dopants

contenant du bore vaporisées ;
l'ionisation desdites espèces de dopants contenant du bore vaporisées dans une chambre à vide dans des conditions d'ionisation pour générer des ions contenant du bore ; et
l'accélération des ions contenant du bore par un champ électrique pour produire un faisceau d'ions pour implanter des ions contenant du bore dans un substrat, dans lequel les espèces de dopants contenant du bore comprennent du B_2F_4.

2. Procédé selon la revendication 1, comprenant en outre le recuit du substrat à la suite de l'implantation des ions contenant du bore dans le substrat.

3. Procédé selon la revendication 1, dans lequel au moins 15 % des espèces de dopants contenant du bore sont ionisés lors de ladite ionisation et ladite ionisation est effectuée à une tension d'arc inférieure à 100 volts en utilisant une source d'ions à cathode chaude.

4. Procédé selon la revendication 3, dans lequel ladite ionisation est effectuée à une tension d'arc inférieure à 90 volts.

5. Procédé selon la revendication 3, dans lequel ladite ionisation est effectuée à une tension d'arc inférieure à 80 volts.

6. Procédé selon la revendication 3, dans lequel ladite ionisation est effectuée à une tension d'arc inférieure à 70 volts.

7. Procédé selon la revendication 1, dans lequel lesdites espèces de dopants contenant du bore sont mélangées avec un gaz noble pour l'ionisation.

8. Procédé selon la revendication 7, dans lequel ledit gaz noble est sélectionné dans le groupe consistant en le néon et l'argon.

9. Procédé selon la revendication 7, dans lequel ledit gaz noble est sélectionné dans le groupe consistant en le krypton et le xénon.

10. Procédé selon la revendication 1, dans lequel lesdites espèces de dopants contenant du bore comprennent en outre du BF_3.

11. Procédé selon la revendication 1, dans lequel ledit substrat comprend un article sélectionné dans le groupe consistant en des substrats semi-conducteurs, des substrats pour des écrans plats, et des substrats pour des systèmes micro-électromécaniques, MEMS.

12. Procédé selon la revendication 1, dans lequel ladite ionisation est effectuée en utilisant une source d'ions.

13. Procédé selon la revendication 12, dans lequel ladite source d'ions comprend une source d'ions sélectionnée dans le groupe consistant en des sources d'ions des types utilisant des thermoélectrodes et alimentées par un arc électrique, des sources d'ions des types hyperfréquences utilisant un magnétron, des sources à cathode chauffée indirectement, et des sources de plasma RF.

14. Procédé selon la revendication 1, dans lequel ladite chambre à vide comprend une électrode d'extraction et ladite ionisation est effectuée pour produire un faisceau d'ions collimaté d'ions contenant du bore.

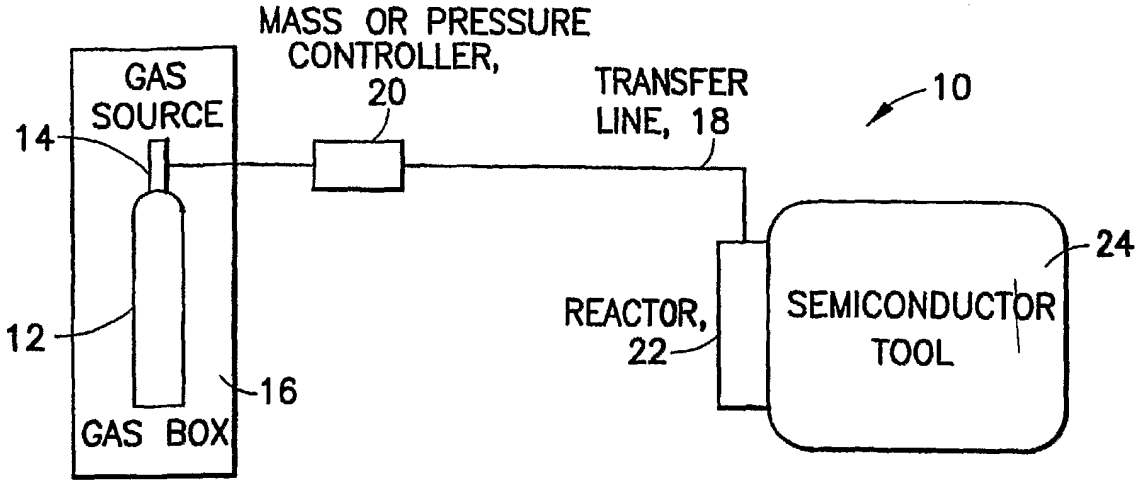

MASS OR PRESSURE
CONTROLLER,
20
GAS
SOURCE
14
TRANSFER
LINE, 18
10
24
12
REACTOR,
22
SEMICONDUCTOR
TOOL
16
GAS BOX

FIG.1

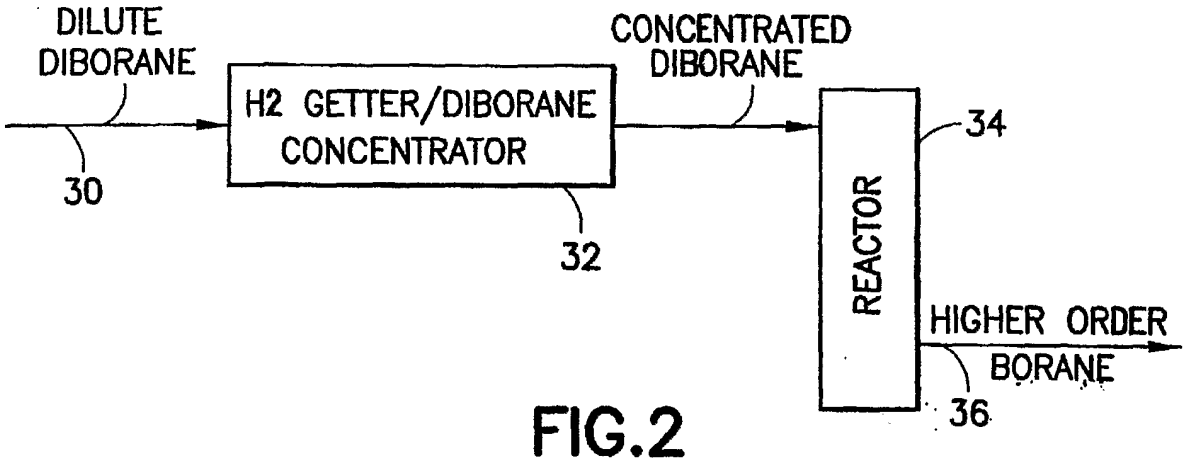

DILUTE
DIBORANE
30
H2 GETTER/DIBORANE
CONCENTRATOR
32
CONCENTRATED
DIBORANE
REACTOR
34
HIGHER ORDER
BORANE
36

FIG.2

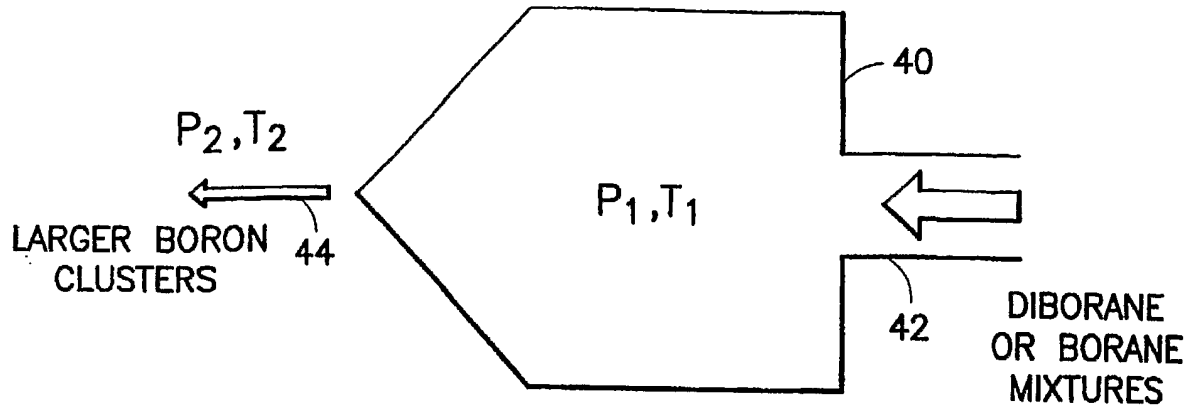

40
P2,T2
P1,T1
LARGER BORON CLUSTERS
44
42
DIBORANE OR BORANE MIXTURES

FIG.3

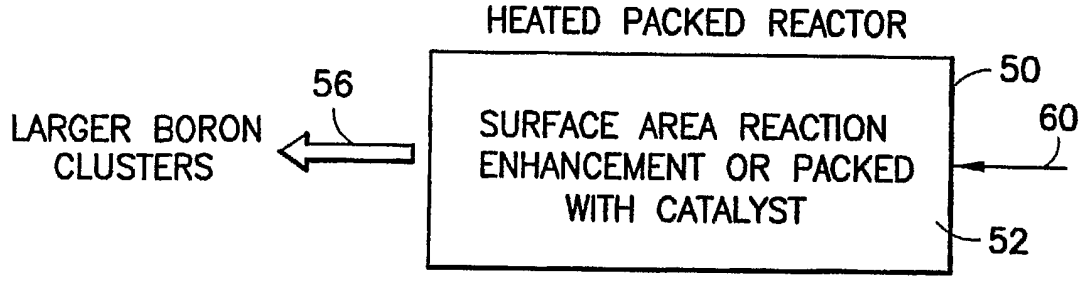

HEATED PACKED REACTOR
56
50
60
LARGER BORON CLUSTERS
SURFACE AREA REACTION ENHANCEMENT OR PACKED WITH CATALYST
52

FIG.4

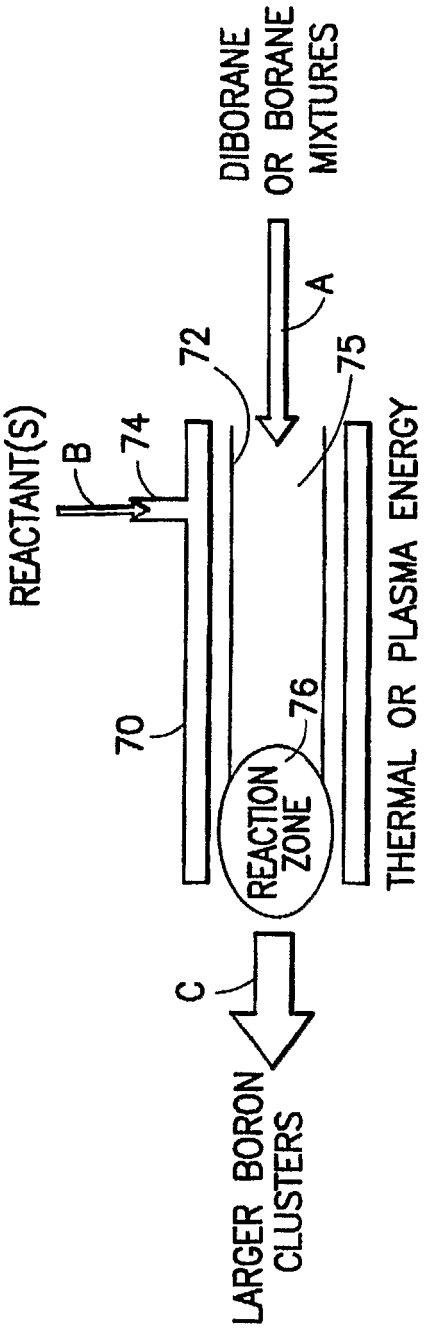

DIBORANE OR BORANE MIXTURES
A
72
75
REACTANT(S)
B
74
70
76
REACTION ZONE
THERMAL OR PLASMA ENERGY
C
LARGER BORON CLUSTERS

FIG.5

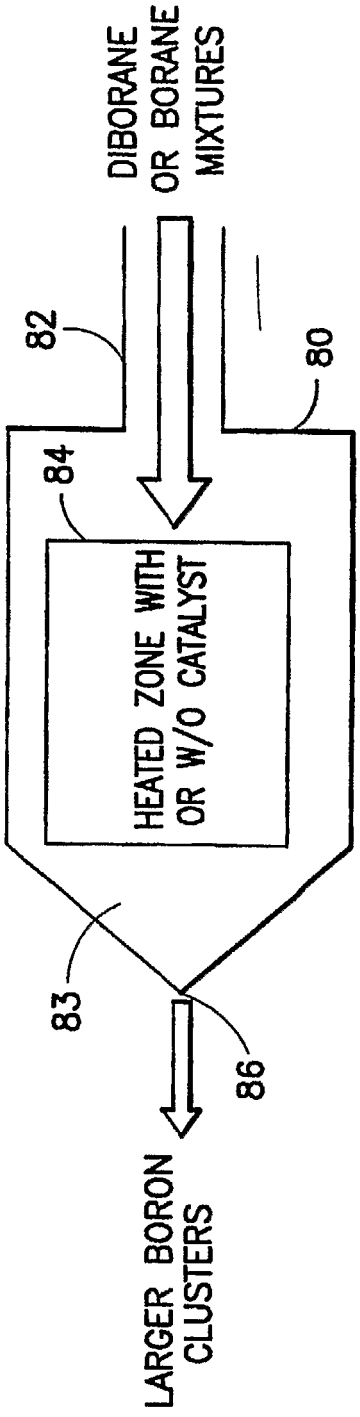

DIBORANE OR BORANE MIXTURES
82
80
84
HEATED ZONE WITH OR W/O CATALYST
83
86
LARGER BORON CLUSTERS

FIG.6

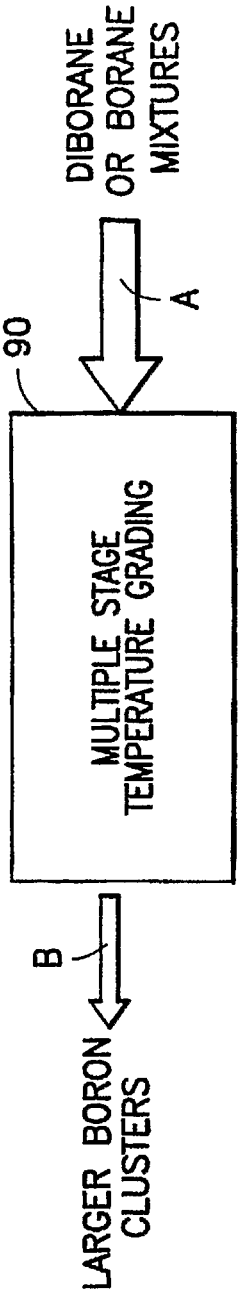

DIBORANE
OR BORANE
MIXTURES
A
90
MULTIPLE STAGE
TEMPERATURE GRADING
B
LARGER BORON
CLUSTERS

FIG.7

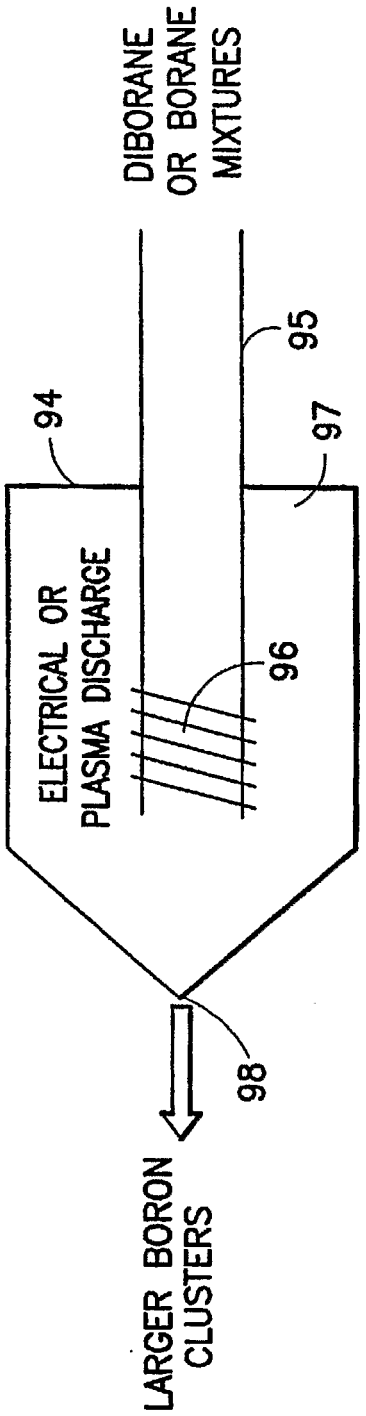

DIBORANE
OR BORANE
MIXTURES
95
94
97
ELECTRICAL OR
PLASMA DISCHARGE
96
98
LARGER BORON
CLUSTERS

FIG.8

REFERENCES CITED IN THE DESCRIPTION

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